

Electronic structure of the ferromagnetic superconductor UCoGe from first principles

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Abstract. The superconductor UCoGe is analyzed with electronic structure calculations using Linearized Augmented Plane Wave method based on Density Functional Theory. Ferromagnetic and antiferromagnetic calculations with and without correlations (via LDA+U_H) were done. In this compound the Fermi level is situated in a region where the main contribution to DOS comes from the U-5f orbital. The magnetic moment is mainly due to the Co-3d orbital with a small contribution from the U-5f orbital. The possibility of fully non-collinear magnetism in this compound seems to be ruled out. These results are compared with the isostructural compound URhGe, in this case the magnetism comes mostly from the U-5f orbital.

Keywords UCoGe, URhGe, superconductivity, electronic structure, magnetism.

1. Introduction

Considerable theoretical and experimental effort has been focused on the interplay of magnetism and superconductivity since it is widely believed that it could help to clarify the mechanism behind high- T_c superconductivity [1]. Particular interest has been put on to the coexistence of ferromagnetism and superconductivity because of the nontrivial phenomena which are predicted or found experimentally, such as the still controversial triplet pairing symmetry found in ferromagnetic superconductors.

After the BCS theory of superconductivity [2, 3], it became clear that pairing of electrons in the singlet state could be destroyed by an exchange mechanism, such as the exchange field in a magnetically ordered state who tends to align spins of Cooper pairs in the same direction preventing a pairing effect. However, experimental evidence has been found of the coexistence of antiferromagnetic order and superconductivity in ternary rare-earth compounds [4]. Superconductivity and antiferromagnetism can coexist, on average, because the exchange and orbital fields are zero at distances of the order of the Cooper pairs size. Later on it was demonstrated that ferromagnetic order is unlikely to appear in the superconducting phase [5, 3]. In spite of this, ferromagnetism was found in superconductors and the first evidence of ferromagnetic

Table 1. Atom positions in the unit cell. The unit cell is orthorhombic with space group $Pnma$ (SG #62), the cell parameters are $a=6.845\text{\AA}$, $b=4.206\text{\AA}$, $c=7.222\text{\AA}$.

	<i>a</i>	<i>b</i>	<i>c</i>
U	0.0101	0.25	0.7075
Co	0.2887	0.25	0.4172
Ge	0.1967	0.25	0.0870

superconductors was given in bulk materials; UGe_2 (at high pressure) [6] and $URhGe$ (at ambient pressure) [7], it has been argued that critical magnetic fluctuations could mediate superconductivity in these compounds.

These systems seem to have triplet paring symmetry which permits the coexistence of superconductivity and ferromagnetism. In this direction, Huy *et al.* [8] recently report, superconductivity on the weak ferromagnet $UCoGe$ at ambient pressure. They claim that superconductivity ($T_c=0.8\text{K}$) and ferromagnetic order ($T_C=3\text{K}$) indeed coexist. They also found an agreement with the triplet pairing scenario in the $UCoGe$ compound. The magnetic moment found by Huy *et al.* for this compound is $M=0.03\mu_B$, which contrasts with the effective paramagnetic moment $M=1.7\mu_B$ [9]. They claim that this material should have band magnetism.

In this paper, spin polarized electronic structure analysis was performed to further understand the $UCoGe$ superconductor. The objective of this analysis is to correlate the particular characteristics of this material with its superconducting properties.

2. Computational details

Electron quantum mechanical calculations were done with the WIEN2k package [10], which is a Linearized Augmented Plane Wave (FP-LAPW) method based on Density Functional Theory (DFT). Spin-orbit coupling is included in a second-variational way, and the strong correlations in uranium were included via LDA+ U_H (SIC) (contributed by Pavel Novák). The Generalized Gradient Approximation of Perdew, Burke and Ernzerhof [11] was used for the treatment of the exchange-correlation interactions. The energy threshold to separate localized and non-localized electronic states was -6 Ry. The muffin-tin radii were: $2.5a_0$ for uranium, $2.43a_0$ for cobalt, $2.48a_0$ for rhodium, and $2.15a_0$ for germanium (a_0 is the Bohr radius). The criterion for the number of plane waves was $R_{MT}^{min} \times K^{max} = 9$ and the number of k-points were 462 ($7 \times 11 \times 6$), for the case with all the atoms independent it was 225 ($5 \times 9 \times 5$). For crystal structure visualization the XCrySDen package [12] was used.

3. Results and discussion

$UCoGe$ has the same crystal structure as $URhGe$ [13, 14], it belongs to the space group $Pnma$ (SG #62). The crystal structure is shown in Figure 1, with the cell parameters taken from Huy *et al.* [8], and the internal atomic positions from Canepa *et al.* [13]. These parameters are shown in Table 1.

The crystal structure is very similar to that of the MgB_2 compound, which consists of B-graphene sheets intercalated with Mg atoms. In the case of $UCoGe$, it is formed of Co-Ge-graphene sheets intercalated with U atoms, as shown in Figure 1 (in the same arrangement as LiBC [15]). The U atoms form chains perpendicular to the graphene

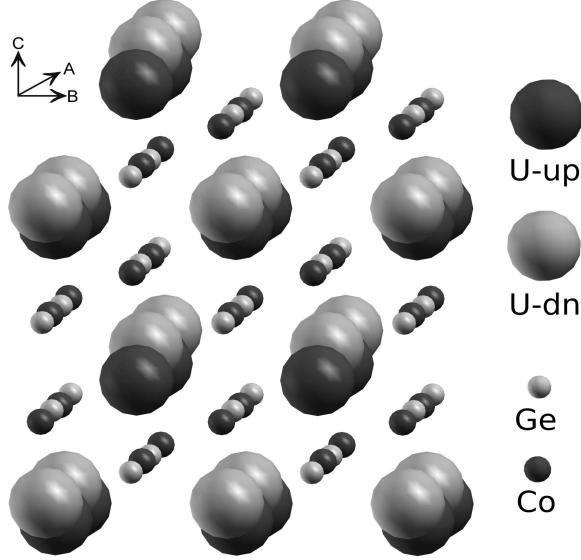


Figure 1. Crystal structure of UCoGe.
U-up and U-dn refer to the antiferromagnetic cell.

sheets, but contrary to MgB_2 and LiBC these chains are not straight but they are in a zigzag arrangement (see Figure 1), and the graphene sheets become corrugated, that is, the Co-Ge-hexagons that are between two U atoms are almost in the plane perpendicular to the U-U line.

Of the U-atoms substructure each U atom has four U neighbours, two along the chain, and other two in contiguous chains. The four neighbours form an unsymmetrical tetrahedron around the central U atom. This situation is similar to C in diamond, that is, the U atoms form a distorted diamond structure.

For electronic structure calculations where there are heavy elements it is important to include spin-orbit interactions, and the magnetization is now dependent of the crystallographic direction. The results show that the most stable magnetization direction is in the c -axis by 3.65meV and 3.00meV with respect to the a - and b -directions respectively, which is the same direction as in URhGe [16, 17].

The magnetic moments are shown in Table 2, the spin components vary little with the crystal direction, but the orbital moments vary considerably. In the c -direction the total moment of the U atom is very small ($M=0.098\mu_B$). The situation of the Co atom is quite different; the orbital moment is quite small but the spin component is fairly large and the total moment does not cancel ($M=0.633\mu_B$), these values are close to those found by Diviš [18], although he found a smaller total moment; $M=0.28\mu_B$. This result is in disagreement with the experimental results of Huy *et al.* [8], in which the total magnetic moment is quite small ($M=0.03\mu_B$), but it is still smaller than the effective paramagnetic moment found by Troć and Tran ($M=1.7\mu_B$) [9]. These results contrast with the case of URhGe , where the Rh atom has a small spin moment and a smaller orbital moment; it is the U atom that has the largest contribution.

The U-5f orbital is fairly localized and there is a strong intra-coulomb repulsion energy, this effect is not normally included in the DFT calculations, but it can be included via a $\text{Hubbard} - U_H$ term ($\text{LDA} + U_H(\text{SIC})$) in the WIEN2k package. The

Table 2. Magnetic moments (μ_B) in the three different directions (only the main orbital component is shown), the last column corresponds to URhGe in the c -direction.

Direction		<i>a</i>	<i>b</i>	<i>c</i>	<i>c</i> (Rh)
Spin term	U	1.088	1.090	1.083	1.037
	Co (Rh)	-0.487	-0.482	-0.472	-0.108
	Ge	-0.028	-0.028	-0.026	-0.026
Orbital term	U	-0.961	-1.105	-1.181	-1.266
	Co (Rh)	-0.058	-0.064	-0.063	-0.011
Sum	U	0.128	-0.016	-0.098	-0.228
	Co (Rh)	-0.546	-0.546	-0.534	-0.119
Total		-0.418	-0.562	-0.633	-0.348

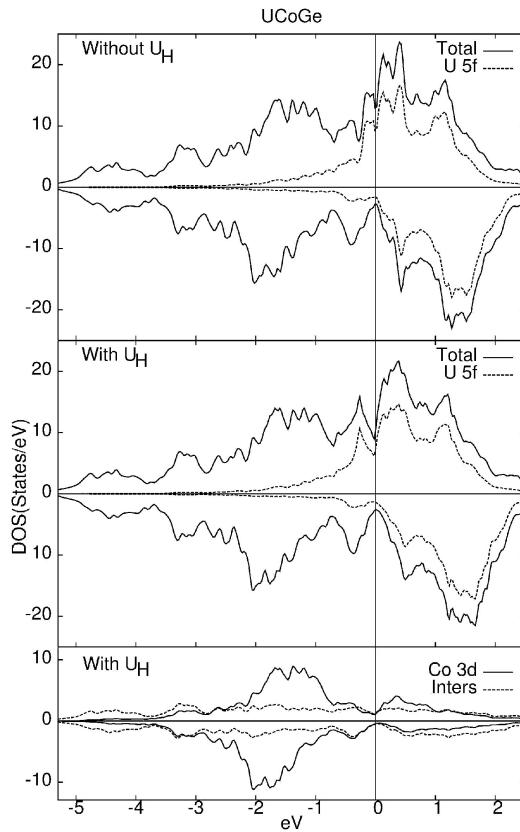


Figure 2. DOS for UCoGe ferromagnetic calculation, up-spin: upward, dn-spin: downward. Top: without U_H correction, middle and bottom with U_H correction. The main contribution at the E_F is from U, at -1.5eV cobalt has a large contribution. Ge has very little contribution everywhere and is not shown.

meaning of the U_H term was discussed by Anisimov and Gunnarsson [19] who defined it as the cost in Coulomb energy by placing two electrons in the same site. They also

Table 3. Magnetic moments (μ_B) of UCoGe and URhGe in the c -direction with U_H -correction (only the c -direction is shown)

Compound		UCoGe	URhGe
Spin term	U	1.175	1.151
	Co/Rh	-0.524	-0.122
	Ge	-0.031	-0.029
Orbital term	U	-1.341	-1.470
	Co/Rh	-0.076	-0.015
Sum	U	-0.167	-0.319
	Co/Rh	-0.600	-0.137
Total		-0.767	-0.456

devised a method of calculating the U_H term from first principles using a supercell. Madsen and Novák [20] adapted this method to the FP-LAPW method (WIEN2k). Using this method the effective U_H ($U_H^{eff} = U_H - J$), for the U-atoms in UCoGe, was found to be $U_H = 0.362$ eV. Rusz and Diviš for UPtAl found that $U_H^{eff} = 0.36$ eV [21] fit the experimental values best. For the other atoms no U_H was used.

With the $LDA + U_H$ correction the magnetic values increase, see Table 3 (for URhGe the same U_H value was used). For UCoGe with this increment the total magnetic moment ($M = 0.767\mu_B$) moves further away from the experimental value of $M = 0.03\mu_B$. On the other hand, the total magnetic moment for URhGe increases to $M = 0.456\mu_B$, which is quite close to the experimental value reported by Aoki *et al.* ($M = 0.42\mu_B$) [7]. For this compound the experimental values vary quite considerably from $M = 0.19\mu_B$ [22] to a value about three times larger [23]. As mentioned above for UCoGe, if both the magnetic ($M = 0.03\mu_B$) and the paramagnetic ($M = 1.7\mu_B$) values are analyzed, the situation is more drastic, and further experimental measurements would narrow this large difference.

Due to the discrepancy between the calculated and small experimental magnetic value in UCoGe, an antiferromagnetic calculation was performed. This is in view of a possible scenario that would explain the small experimental total magnetic moment; in an antiferromagnetic configuration the individual magnetic moments are antiparallel and the total magnetic moment is zero. If these moments are not exactly antiparallel but slightly canted then they would not cancel exactly and a small perpendicular moment would remain, this would explain the small experimental value.

The U atoms that form a distorted diamond structure can be separated into U-up and U-dn now with a distorted zincblende structure, the new crystal structure belongs to the space group $Pnm2_1$ (SG #31). The collinear antiferromagnetic configuration with the magnetic moment in the c -direction was calculated. The energy was found to be 33.2meV higher than that of the ferromagnetic configuration. The canted configuration should not be very different from the collinear one in terms of energy (the angle would be of $\sim 4.3^\circ$), therefore the canted antiferromagnetic configuration can be ruled out, and the ferromagnetic configuration with the magnetization in the c -direction is the most stable configuration.

Electronic structure calculation for the ferromagnetic structure with the magnetic moments in the c -direction (Figure 1) shows that all the atomic bonds are mostly metallic, that is, the charge density is around the atoms and has an almost spherical

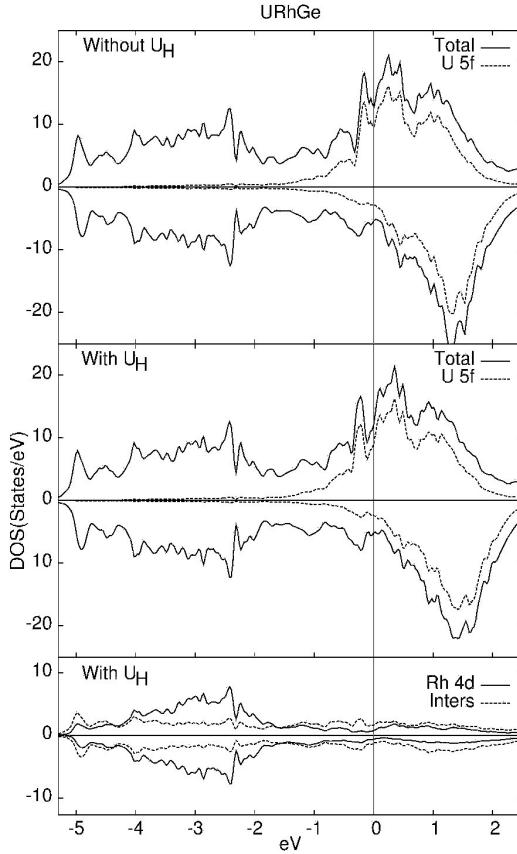


Figure 3. DOS for URhGe ferromagnetic calculation, rhodium has a small contribution at E_F .

shape, in the interstitial space the density is fairly homogeneous. The main contribution to the *Density of States* (DOS) (Figure 2) comes from U that is mostly U-5f followed by Co that is mostly Co-3d. There is a large U peak at E_F [-0.8eV, 2eV], Co has a large contribution at \sim -1.5eV, but still close enough to E_F and Co has an important magnetic moment. The Ge contribution, not shown, is very small, there is an important contribution from the interstitial space. DOS at E_F is quite large for up-spin and it is small for down-spin, when the U_H -correction is introduced a small gap begins to form for up-spin. DOS for URhGe, Figure 3, shows that the Rh-4d is at much lower energy, \sim -3eV, and the magnetic moment is considerably smaller than in UCoGe.

Other possibility to obtain the experimental $M=0.03\mu_B$ value would be to have non-collinear magnetism. UCoGe has four formula units in the unit-cell. To test the possibility of non-collinear magnetic order a calculation using the WIEN2k was done but with all the atoms in the unit-cell independent, that is, each atom could have different values, in particular they could have a different magnetic moment directions. WIEN2k is not fully non-collinear, but it can give deviations of the magnetic moments from the main magnetization direction [17]. If as a result of this calculation large

Table 4. Magnetic moments (μ_B) of UCoGe with the principal magnetization in the a -direction, with all the atoms independent, the canting is in the c -direction

Component	Spin	Orbital	
Canting		(c)	(c)
U	1.133	-0.032	-0.991
	1.224	0.028	-1.183
	1.223	-0.029	-1.183
	1.133	0.032	-0.994
Co	-0.498	0.001	-0.044
	-0.534	0.005	-0.124
	-0.533	-0.005	-0.124
	-0.499	-0.001	-0.044

Table 5. Magnetic moments (μ_B) of UCoGe with all the atoms independent, the canting direction is in parenthesis

Direction	a	b	c	
Canting		(c)		(a)
U	0.142	0.109	-0.113	-0.073
	0.042	-0.180	-0.108	-0.287
	0.040	0.180	-0.114	-0.072
	0.139	-0.108	-0.107	-0.287
Tot/f.u.	0.091	0	-0.111	-0.180
Co	-0.542	-0.004	-0.613	-0.616
	-0.658	-0.004	-0.611	-0.596
	-0.657	0.004	-0.610	-0.615
	-0.543	0.004	-0.615	-0.596
Tot/f.u.	0.600	0	-0.612	-0.606
Tot/f.u.	0.691		-0.723	-0.786

deviations are obtained then the system should have fully non-collinear magnetism, on the other hand, if only small deviations are obtained then UCoGe would have a main magnetization direction with the magnetic moments slightly canted.

With all the atoms independent the symmetry is reduced drastically, the new space group is Pm (SG #6). There is no inversion symmetry and complex numbers need to be used, this increases fivefold the computation time. In the new cell the crystal axes are different from the original ones, but to avoid confusion the original axes will be used.

Now the most stable magnetization direction is in the b -direction, the a - and c -directions are higher in energy by 8.7meV and 0.8meV respectively.

The spin and orbital moments of the case with the main magnetization in the a -direction are shown in Table 4, the sums are shown in Table 5. The U spin moments are relatively large, but they are almost compensated with the orbital moment. The Co spin moments are smaller, in this case the orbital moments are considerably smaller and with the same sign. The canting (deviation from the main direction) of the spin terms is very small, the largest corresponds to $U_1=1.6^\circ$. The canting of the orbital terms are larger, the largest is $U_3=10^\circ$.

The c -direction case shows similar trends, although the U orbital moments are

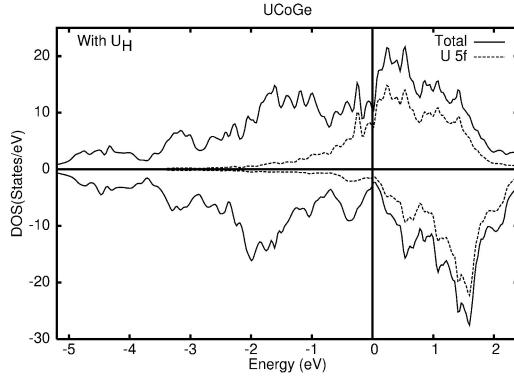


Figure 4. DOS for UCoGe ferromagnetic calculation with all atoms in the unit cell independent; up-spin: upward, dn-spin: downward.

larger than the spin moments and the system becomes ferromagnetic with the U and Co magnetic moments pointing in the same direction. Again, the canting of the spin moments is quite small $<2^\circ$. For the U atoms the canting of the orbital terms is smaller $\sim 5^\circ$, for the Co atoms the canting angle is considerably larger $Co_3=20^\circ$, but this is due to the very small value in the *c*-direction ($0.099\mu_B$). In the *b*-direction case, the most stable, again the U orbital moment is larger than the spin term, in this case, due to symmetry, the magnetization is fully collinear (there is no canting).

These results show that in the most stable case there is no canting, while in the others, not far above, the canting is quite small $<10^\circ$, with the exception of *c*-direction orbital term $Co_3=20^\circ$ which, as explained above, is due to the smallness of the main term. All these results show that UCoGe does not have a fully non-collinear magnetism; all the magnetic moments are aligned, parallel or antiparallel, to a main direction with only small deviations.

The sums of the spin and orbital terms for the three magnetization directions are shown in Table 5. As it can be seen there are no large differences with the original case where all the atoms of same kind were equivalent. There is an interesting difference though; in the latter case not all the moments of each atom are the same, they are split into two groups, also the canting is in opposite directions, still all the charges of equal atoms were found to be the same.

A possible cause of the differentiation of the magnetic values could be due to the large slope, in the initial case, in the up-spin DOS at E_F , which is an unstable situation. Given the freedom, in the latter case, the magnetic moments rearrange and the partial gap is reduced and widened (Figure 4).

Fermi surfaces (FS), that are the bands at E_F , give information about the electrical conductivity; the electrons move perpendicular to the FS. For parabolic bands it can be easily proven that the conductivity is proportional to the volume within the FS[24], this can be applied to FS near the band edges, when the bands can be approximated to parabolas.

In UCoGe there are two large up-spin FS (Figure 5), and the material should be a good conductor, in this case it would rule out a phononic mechanism. These FS are touching and the possibility of multiple gaps is unlikely due to interband scattering. One of the up-spin FS is an undulated plane perpendicular to the U-chains, the main conductivity from this FS would be along these U-chains (Figure 5, up-spin, top and

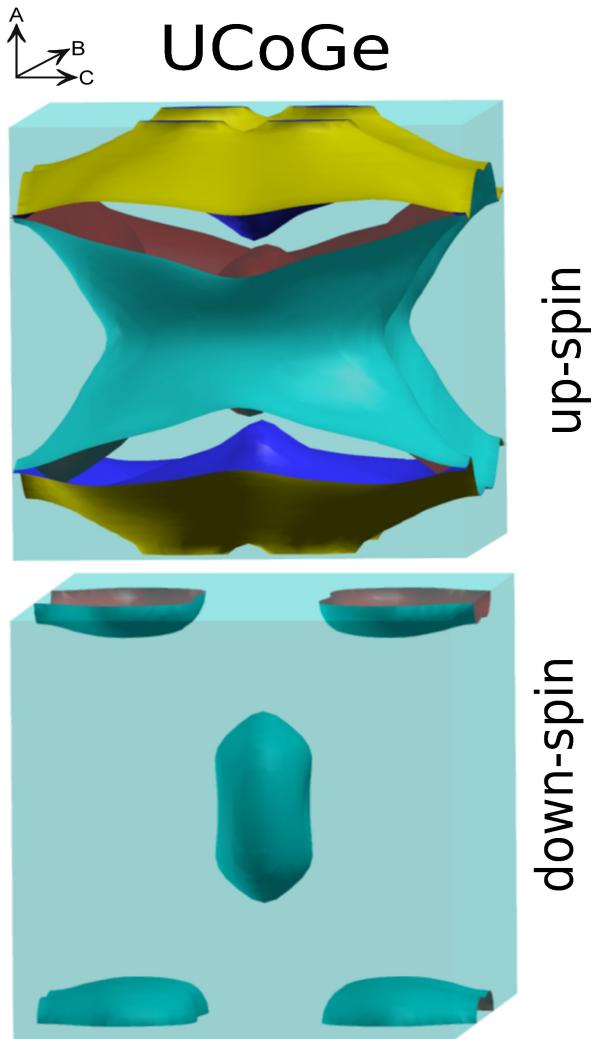


Figure 5. Fermi surfaces of UCoGe.
above: up-spin, below: down-spin.

bottom FS).

For down-spin it is found that E_F is close to the upper band-edge, DOS has a low value and there are two fairly small FS, all these imply that the down-spin conductivity is quite low and this material would be close to a half-metal.

In the case of URhGe there are large FS in both spin directions, in this case they are clearly separated, but still close from each other, therefore URhGe seems to be a good conductor and probably without multiple gaps. It has a magnetic moment, but in this case it is the U-5d orbital that makes the principal contribution to the magnetism.

4. Conclusion

Spin polarized electronic structure calculations offer a panorama that is essential for the understanding of the coexistence of superconductivity and ferromagnetism in UCoGe. These calculations show that UCoGe is a multiband ferromagnetic superconductor with a magnetic moment that is not small which is mainly due to the Co atom. The antiferromagnetic configuration has a higher energy, also it has been shown that the possibility of fully non-collinear magnetism is unlikely, the magnetic moments point towards a definite direction with only small deviations. The large up-spin Fermi surfaces show that it is a good conductor, probably ruling out a phononic mechanism, it has small down-spin Fermi surfaces and the compound is close to be a half metal. In the isostructural compound URhGe the magnetic moment is mostly due to the U atom.

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